Synthesis, structure, and reactivity of electron-deficient zirconium and hafnium polyhydride complexes

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2 Pentamethylcyclopentadienyl Zirconium and Hafnium *N*,*N*-dimethylaminopropyl Alkyl Complexes and Their Conversion to Polyhydride Complexes*

Group 4 metal metallocene hydride species are used for stoichiometric[1] as well as catalytic[2] reductions of organic substrates. The synthesis and organometallic chemistry of these metallocene hydrides has been investigated quite extensively, especially for zirconium.[3-6] Relatively little is known on the synthesis and chemistry of non-metallocene group 4 metal hydrides.[7-11]

The synthesis of group 4 metal hydrides is usually performed either by reaction of metal halide species with boron hydrides or trialkyl tin hydrides, or by hydrogenolysis of metal alkyl species. The first route has led to a number of interesting mixed group 4 metal-boron polyhydride species,[7] but it is difficult to obtain boron-free compounds. A range of polynuclear mixed hydrido-halide zirconium species were obtained by reaction of zirconium halides with trialkyl tin hydrides in the presence of phosphines.[11] Hydrogenolysis of simple mono(pentamethyl)cyclopentadienyl group 4 metal alkyl species such as $Cp^*M(CH_3)_nCl_{3-n}$ has not yielded well-defined products so far, producing mostly poorly soluble materials.[10] Only when bulky phosphido ligands were used in the starting materials could complexes such as $[Cp^*Hf(R)(\mu\text{-}P\textit{t}Bu_2)(\mu\text{-}H)]_2$ (R = Cl, Me) be obtained.[10b]

The observation, made previously in our group, that hydrogenolysis of the hafnium 2,3-dimethyl-1,3-butadiene complex $Cp^*Hf(C_6H_{10})Cl$ yields a soluble, well-defined tetrameric hydride, $[Cp^*Hf(H)_2Cl]_4$,[12] suggested that the nature of the hydrocarbyl precursor is of crucial importance for the formation of well-defined soluble polyhydride species. The *N*,*N*-dimethylaminopropyl ligand, with an amine substituent that can provide (transient) intramolecular stabilization, was expected to have favorable properties in this respect, and exploratory results were

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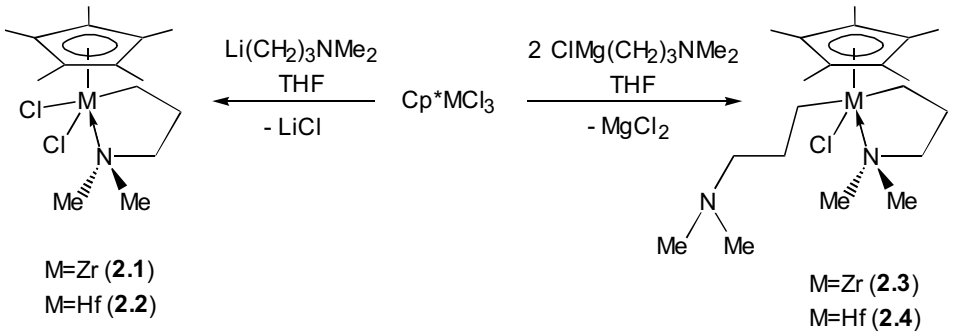
published for zirconium.[13] In this Chapter the synthesis of the alkyl compounds $Cp^*M[(CH_2)_3NMe_2]_nCl_{3-n}$ (M = Zr, Hf; n = 1, 2, 3) and $M[(CH_2)_3NMe_2]_4$ and their use in generating well-defined polyhydride complexes will be described.

2.1 Synthesis of zirconium and hafnium *N*,*N*-dimethylaminopropyl complexes.

The zirconium *N*,*N*-dimethylaminopropyl complexes $Cp^*Zr[(CH_2)_3NMe_2]Cl_2$ (**2.1**) and $Cp^*Zr[(CH_2)_3NMe_2]_2Cl$ (**2.3**) were previously described.[13] Reaction of Cp^*ZrCl_3 with two equivalents of $ClMg(CH_2)_3NMe_2$ gave the dialkyl **2.3**. Complex **2.1** was obtained by a ligand redistribution reaction between **2.3** and Cp^*ZrCl_3.

Both Zr and Hf monoalkyl complexes $Cp^*M[(CH_2)_3NMe_2]Cl_2$ ($Cp^* = \eta^5$-C_5Me_5, M = Zr, **2.1**; Hf, **2.2**) could also be obtained directly from the reaction of Cp^*MCl_3 with 1 equiv of $Li(CH_2)_3NMe_2$ in THF in 65% isolated yield (Scheme 2.1). The hafnium dialkyl complex $Cp^*Hf[(CH_2)_3NMe_2]_2Cl$ (**2.4**) was most conveniently prepared by the reaction of Cp^*HfCl_3 with 2 equiv of the corresponding Grignard reagent $ClMg(CH_2)_3NMe_2$ (Scheme 2.1). Mixtures of the monoalkyl and dialkyl complexes were obtained when 2 equiv of the alkyllithium reagent were used.



Scheme 2.1. Synthesis of monoalkyl and dialkyl complexes

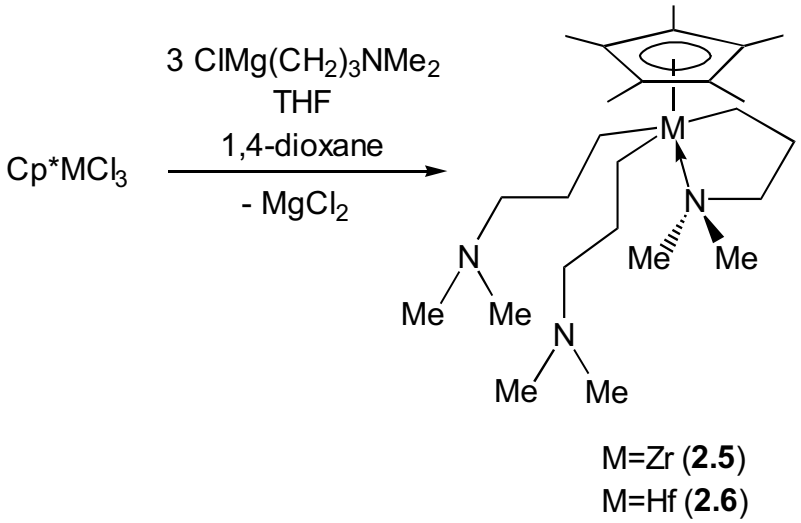
The ^1H NMR spectra of the monoalkyl complexes **2.1** and **2.2** each show a single resonance for the NMe_2-group, which does not show coalescence broadening even down to –60 ºC. This indicates either a pseudo trigonal-bipyramidal geometry of the complex with C_s symmetry, or a very rapid rotation and inversion of the NMe_2-group on the NMR time scale. The IR spectra of the

dialkyls **2.3** and **2.4** show a ν_{CH} absorption around 2760 cm^{-1}, indicative of a non-coordinated NMe_2-group,[14] which is absent in the IR spectra of the monoalkyls **2.1** and **2.2**. This suggests that in all the alkyl complexes **2.1**-**2.4** one dimethylaminopropyl group is chelating. At 20 ºC the 500 MHz ^{1}H NMR spectra of the dialkyls **2.3** and **2.4** are indicative of a symmetrically averaged structure, but at –60 ºC the fluxionality is slow on the NMR timescale for the Hf dialkyl complex **2.4**. All α-methylene protons are inequivalent at that temperature, and the NMe_2 resonance is split into three resonances in a 3:3:6 ratio. At this temperature the fluxionality in the Zr complex **2.3** has not yet reached the slow exchange limit. From the coalescence temperatures for one of the MCH_2 groups the free energy of activation $\Delta G^{\ddagger}_{Tc}$ of this process was estimated to be 43.9 ± 0.2 $kJmol^{-1}$ (at T_c = –46 ± 1 ºC) for **2.3** and 45.8 ± 0.6 $kJmol^{-1}$ (at T_c = –36 ± 1 ºC) for **2.4**.[15] These NMR data indicate that in the dialkyl species only one dimethylaminopropyl group is chelating at a time, which is consistent with the IR data.

The trialkyl complexes $Cp^*M[(CH_2)_3NMe_2]_3$ (M = Zr, **2.5**; Hf, **2.6**) were most conveniently prepared by the reaction of Cp^*MCl_3 with 3 equiv of the corresponding Grignard reagent $ClMg(CH_2)_3NMe_2$ in the presence of 3 equiv of 1,4-dioxane (Scheme 2.2). The complexes were obtained as oils at ambient temperature, in high yield (with for **2.6** as a significant observable impurity the dialkyl complex **2.4** (18%)). Attempts to purifiy these compounds by recrystallization from pentane at –60 ºC were not successful, as the solid deposited at that temperature readily melted again upon work-up. When the alkylation reaction was performed without the addition of dioxane, a mixture was obtained of the dialkyl complex **2.4** (30%), the trialkyl complex **2.6** (30%) and an unknown species (40%) with a very broad ^{1}H NMR resonance at δ 0.45 ppm (which may be attributed to a Mg-containing species).

At 20 ºC the 500 MHz ^{1}H NMR spectra of the trialkyls **2.5** and **2.6** are indicative of a symmetrically averaged structure. Cooling an NMR tube with a solution of **2.5** to –90 ºC reveals that at this temperature the fluxionality in the complexes has not yet fully reached the slow exchange limit. Nevertheless, the $ZrCH_2$ resonance at δ 0.20 ppm is split into three broad resonances (δ 0.51, 0.36, and –0.11 ppm) at this temperature, as is expected for the structure of **2.5** as shown in Scheme 2.2, although the coupling constants are not yet resolved. For **2.6** the slow exchange limit has not been reached at –90 ºC. The IR spectra of the trialkyls **2.5** and **2.6** also show a ν_{CH} absorption around 2760 cm^{-1}, indicative of a

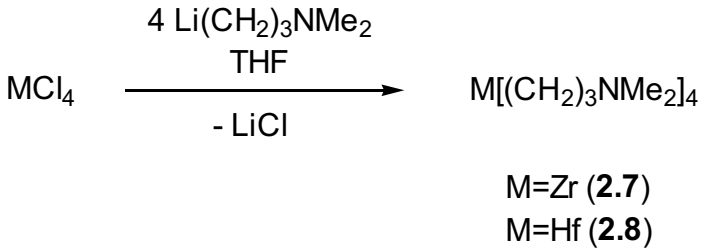
non-coordinated NMe_2-group.[14] It is likely that, in analogy to the dialkyls **2.3** and **2.4**, only one of the dimethylamino groups is coordinated to the metal center.



Scheme 2.2. Synthesis of trialkyl complexes

The homoleptic complexes $M[(CH_2)_3NMe_2]_4$ (M = Zr, **2.7**; Hf, **2.8**) were synthesized from MCl_4 and 4 equiv of the alkyl-lithium reagent in THF (Scheme 2.3). The complexes were obtained as oils (**2.7** brown, **2.8** pale yellow) in nearly quantitative yield. Attempts to recrystallize **2.7** and **2.8** at –60 ºC were not successful, as the solid deposited at that temperature readily melted again upon work-up. For M = Zr a synthesis procedure has been described in the literature using Et_2O as solvent,[16] and from which **2.7** was obtained as colorless crystals, but without a specified yield. When the reaction with M = Zr was repeated under these conditions, no crystalline material was obtained. The ^{13}C NMR spectrum was reported for **2.7** as showing only a single set of four resonances for the alkyl groups. From this it was concluded by the authors that all four N atoms are coordinated to the metal center. However, in the dialkyl complexes **2.3** and **2.4** and the trialkyl complexes **2.5** and **2.6** a fluxional process causes the room temperature spectrum to be that of an averaged structure. We therefore feel that the conclusion of the authors based solely on the room temperature ^{13}C spectrum is not necessarily correct.

At 20 ºC the ^1H NMR spectra of the tetraalkyls **2.7** and **2.8** show four resonances for the *N*,*N*-dimethylaminopropyl ligand (one methyl and three methylene resonances), in the same region as those for **2.1**-**2.6**.



Scheme 2.3. Synthesis of homoleptic alkyl complexes

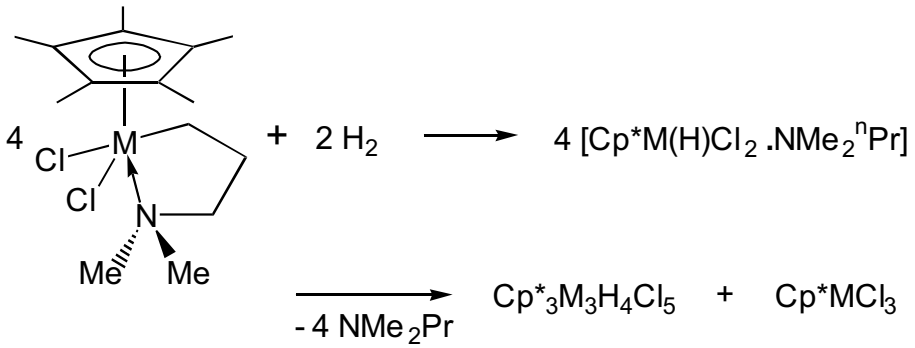
Ligand exchange reactions were performed between $Zr[(CH_2)_3NMe_2]_4$ and $ZrCl_4$ to prepare the various mixed alkyl/chloride derivatives. Reaction of 1 equiv of **2.7** with 1 equiv of $ZrCl_4$ (benzene-d_6 solvent) gave 2 equiv of $Zr[(CH_2)_3NMe_2]_2Cl_2$ (**2.9**) The ^{1}H NMR spectrum of **2.9** at 20 ºC again shows a single set of four resonances; a singlet for the NMe_2 group at δ 2.36, a triplet for the NCH_2 at δ 2.62, a multiplet for the CH_2 at δ 1.96 and a multiplet for the $ZrCH_2$ at δ 1.56 ppm. These resonances are shifted downfield, especially the $ZrCH_2$ and NCH_2 resonances, compared to the resonances of the tetraalkyl complex **2.7**. Compound **2.9** is not stable in solution at room temperature, and readily decomposes in a few hours, releasing free (*n*-propyl)dimethylamine (^{1}H NMR). Compund **2.9** was obtained on a 1.70 mmol scale as a brown solid. The ^{1}H NMR spectrum of isolated **2.9** (toluene-d_8 solvent) always showed the presence of some free amine. It did not show coalescence broadening of the metal alkyl resonances down to −60 ºC, although upon cooling the resonances shifted slightly upfield, especially for the NCH_2 and NMe_2 protons. This may indicate a rapid equilibrium between structures. When 3 equiv of **2.7** were reacted with 1 equiv of $ZrCl_4$, or 1 equiv of **2.7** with 3 equiv of $ZrCl_4$ (benzene-d_6 solvent), the resulting products were found to be highly unstable at ambient temperature. The ^{1}H NMR spectra of these mixtures show resonances for the free amine, together with some very broad resonances between 1.5-2.5 ppm.

Mixed $Cl_nZr[(CH_2)_3NMe_2]_{4-n}$ complexes can thus be generated by ligand exchange reactions, but they are not stable enough to be isolated in pure form. For this reason their hydrogenolysis has not been studied.

2.2 Hydrogenolysis of the *N*,*N*-dimethylaminopropyl complexes.

Reaction of the monoalkyl complexes **2.1** and **2.2** with H_2 (benzene-d_6 solvent) at ambient temperature and pressure resulted in clear, pale yellow solutions.

Monitoring the reactions by ^{1}H NMR spectroscopy revealed gradual formation of free (*n*-propyl)dimethylamine, Cp*MCl_3 and a polyhydride species with three inequivalent Cp* groups and four inequivalent hydrides. For Zr, it was reported that the reaction takes about 24 h at ambient temperature to go to completion.[13] For Hf this takes about 48 h. The hydride resonances for the Zr compound are found at δ 4.23, 3.92, 2.96, and 0.88 ppm, for the Hf congener at δ 9.17, 8.46, 7.71, and 4.63 ppm, with each resonance integrating as a single hydride. Based on the NMR data, as well as elemental analysis and X-ray diffraction data for the compound with M = Hf (*vide infra*), these products are formulated as Cp*$_3$$M_3H_4Cl_5$ (M = Zr, **2.10**; Hf, **2.11**; Scheme 2.4).



Scheme 2.4. Synthesis of the trinuclear polyhydride complexes Cp*$_3$$M_3H_4Cl_5$

Warming the solutions of the polyhydrides in the NMR spectrometer revealed complicated fluxional behavior for compounds **2.10** and **2.11**. Initially, the two upfield Cp* signals coalesce into a single resonance (around 40 ºC). At about 70 ºC the third Cp* signal also broadens significantly, but the full fast exchange limit could not be reached for either compound (100 ºC). The three downfield hydride resonances also collapse, and at elevated temperature the upfield hydride signal broadens as well.

From reactions on a 1.5-2.5 mmol scale (toluene solvent) the polyhydrides could be isolated as crystalline material by slow diffusion of pentane or hexane into the solution. It previously proved difficult to obtain the Zr derivative **2.10** analytically pure due to cocrystallization of Cp*$ZrCl_3$.[13] A structural characterization of **2.10** was hampered by facile loss of cocrystallized solvent from the crystal lattice, rendering the material unsuitable for X-ray analysis. In contrast, the Hf-analogue **2.11** was isolated analytically pure in 80% yield from

this procedure, and suitable crystals were obtained for an X-ray structure determination.

The crystal structure of **2.11** (Figure 2.1, pertinent interatomic distances and angles in Table 2.1) reveals a triangular trinuclear arrangement, with each Hf atom bearing one η^5-Cp* ligand and one terminal chloride. Two sides of the cluster, Hf(1)Hf(2) and Hf(2)Hf(3), are bridged by one chloride ligand. The three metal-metal distances are all quite different, Hf(2)…Hf(3) being the longest, 3.721(7) Å (with a bridging chloride), and Hf(1)…Hf(3) the shortest, 3.061(6) Å (without a bridging chloride). The hydrides were not located from the difference Fourier map, but the structural features of **2.11**, calculations performed on a model for **2.11** (*vide infra*) and the spectroscopic data of **2.11** allow a proposal to be made for their positions.

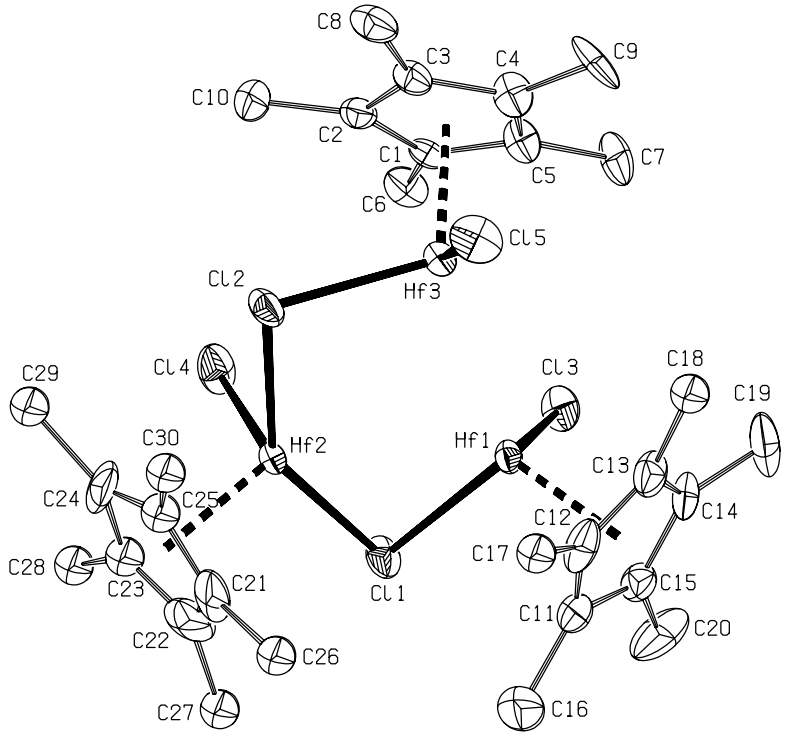


Figure 2.1. Molecular structure of $Cp^*_3Hf_3H_4Cl_5$ (**2.11**) showing 50% probability ellipsoids. For a better visualization the atoms C17, C18, C23 and C25-C30 are represented isotropically.

Table 2.1. Selected bond distances (Å) and angles (deg) for $Cp^*_3Hf_3H_4Cl_5$ (**2.11**).

Hf(1)…Hf(2)	3.241(6)	Hf(2)-Cl(1)	2.516(3)
Hf(2)…Hf(3)	3.721(7)	Hf(2)-Cl(2)	2.536(3)
Hf(1)…Hf(3)	3.061(6)	Hf(3)-Cl(2)	2.514(3)
Hf(1)-Cg	2.473	Hf(1)-Cl(3)	2.470(3)
Hf(2)-Cg	2.472	Hf(2)-Cl(4)	2.394(3)
Hf(3)-Cg	2.484	Hf(3)-Cl(5)	2.399(3)
Hf(1)-Cl(1)	2.648(3)		
Hf(1)-Cl(1)-Hf(2)	77.71(7)	Cl(1)-Hf(2)-Cl(4)	89.91(10)
Hf(2)-Cl(2)-Hf(3)	94.93(10)	Cl(2)-Hf(2)-Cl(4)	92.18(10)
Cl(1)-Hf(1)-Cl(3)	79.24(9)	Cl(2)-Hf(3)-Cl(5)	93.59(10)
Cl(1)-Hf(2)-Cl(2)	143.11(9)		

The Hf(1)…Hf(3) distance in **2.11** (3.061(6) Å) is close to the Zr(1)…Zr(2) distance (3.126(1) Å) in the Zr(μ-H)$_3$Zr dimer $Cp^*_2Zr_2(\mu\text{-H})_3Cl_3(PMe_3)$.[13] Therefore, it seems reasonable to propose that Hf(1) and Hf(3) are connected by three bridging hydrides. The two remaining Hf…Hf sides in triangular **2.11** are each bridged by one chloride. The Hf(2)…Hf(3) distance of 3.721(7) Å is quite long, and close to the intermetallic distances observed in Hf(μ-Cl)$_2$Hf units (3.9-4.0Å).[17] It seems unlikely that Hf(2) and Hf(3) are bridged by a hydride as well as by a chloride ligand. The Hf(1)…Hf(2) distance of 3.241(6) Å is much closer to known intermetallic distances in $Hf_2(\mu\text{-H})_2$ units, for example, the Hf…Hf distance of 3.397 Å in the Hf(μ-H)$_2$Hf dimer [Cp*Hf(*i*Pr-DAB)(μ-H)]$_2$ (*i*Pr-DAB = *N*,*N*'-diisopropyl-1,4-diaza-1,3-butadiene).[18] It thus seems possible that Hf(1) and Hf(2) in **2.11** are bridged by one chloride and one hydride.

DFT Calculations on the model hydride trimers $(\eta^5\text{-}C_5H_5)_3M_3H_4Cl_5$ (M = Zr, Hf) were performed by Dr. A. Ehlers at the VU, Amsterdam. The experimentally obtained positions of the heavy atoms of **2.11** (hafnium, chlorine and carbon) were used as starting points for the geometry optimization of the compound and the hydride atoms were projected into bridging positions between two metal centers. The lowest energy structure that was found shows one hydride in a μ_3-position, bridging over the three metal centers. The calculated geometrical parameters are listed in Table 2.2.

Table **2.2**. Calculated bond lengths (Å) and angles (deg) of $(\eta^5\text{-}C_5H_5)_3M_3H_4Cl_5$ (M = Zr, Hf), compared to the experimental values of **2.11**.

	M=Zr	M=Hf	M=Hf (exp; **2.11**)
M(1)-M(2)	3.293	3.263	3.241(6)
M(2)-M(3)	3.774	3.762	3.721(7)
M(1)-M(3)	3.132	3.082	3.061(6)
M(1)-H(1)	2.019	2.005	-
M(1)-H(2)	2.015	2.015	-
M(1)-H(3)	1.954	1.955	-
M(1)-H(4)	2.071	2.049	-
M(2)-H(2)	1.970	1.963	-
M(2)-H(4)	2.168	2.170	-
M(3)-H(1)	1.936	1.927	-
M(3)-H(3)	1.979	1.965	-
M(3)-H(4)	2.111	2.100	-
M(1)-Cg	2.511	2.457	2.473
M(2)-Cg	2.512	2.518	2.472
M(3)-Cg	2.509	2.534	2.484
M(1)-Cl(1)	2.692	2.719	2.648(3)
M(2)-Cl(1)	2.531	2.543	2.516(3)
M(2)-Cl(2)	2.605	2.614	2.536(3)
M(3)-Cl(2)	2.589	2.592	2.514(3)
M(1)-Cl(3)	2.474	2.494	2.470(3)
M(2)-Cl(4)	2.417	2.430	2.394(3)
M(3)-Cl(5)	2.406	2.419	2.399(3)
M(1)-H(2)-M(2)	111.4	110.2	-
M(1)-H(4)-M(2)	101.9	101.3	-
M(1)-H(1)-M(3)	104.7	103.2	-
M(1)-H(3)-M(3)	105.6	103.7	-
M(1)-H(4)-M(3)	97.0	95.9	-
M(2)-H(4)-M(3)	123.8	123.5	-
M(1)-Cl(1)-M(2)	78.1	76.6	77.71(7)
M(2)-Cl(2)-M(3)	93.2	92.5	94.93(10)
Cl(1)-M(1)-Cl(3)	80.9	79.7	79.24(9)
Cl(1)-M(2)-Cl(2)	142.9	143.5	143.11(9)
Cl(1)-M(2)-Cl(4)	93.7	92.8	89.91(10)
Cl(2)-M(2)-Cl(4)	92.6	92.9	92.18(10)
Cl(2)-M(3)-Cl(5)	100.6	99.9	93.59(10)

The theoretically predicted bond lengths and angles are in good agreement with the experimentally observed ones. The metal-hydride distances of the μ_3-bridging H(4) are slightly longer (Zr: 2.071-2.168 Å, Hf: 2.049-2.170 Å) than those of the μ_2-bridging hydrides (Zr: 1.954-2.019 Å, Hf: 1.955-2.005 Å). The metal-metal distances for **2.11** are slightly shorter than those for **2.10**, due to the smaller atomic radius of hafnium.

The proposed structure for **2.11** is shown in Figure 2.2. The Hf(1)–Cl(3) bond is the longest of the three Hf–$Cl_{terminal}$ bonds and the Cl(1)–Hf(1)–Cl(3) and Cg–Hf(1)–Cl(3) angles are the smallest of the $Cl_{bridging}$–Hf–$Cl_{terminal}$ and Cg–Hf–$Cl_{terminal}$ angles. This indicates that Hf(1) has a higher coordination number than the other two Hf centers, in agreement with the proposed structure. The NMR data are also in accordance with the proposed structure. In the complex $\{[Cp_2Y(\mu_2\text{-}H)]_3(\mu_3\text{-}H)\}\{Li(THF)_4\}$ the resonance for the μ_3-hydride (δ −1.03 ppm) is found upfield from those of the μ_2-hydrides (δ 0.75 ppm).[19] The same trend is found in $[Cp^*_2ZrH_3Li]_3$.[20]

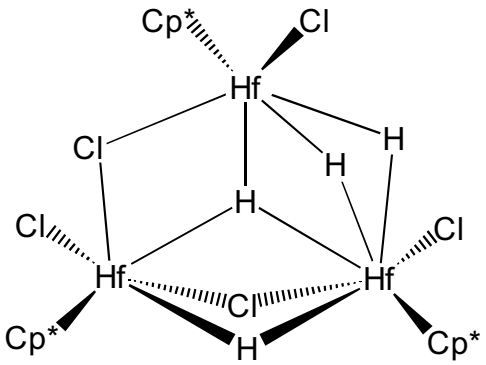
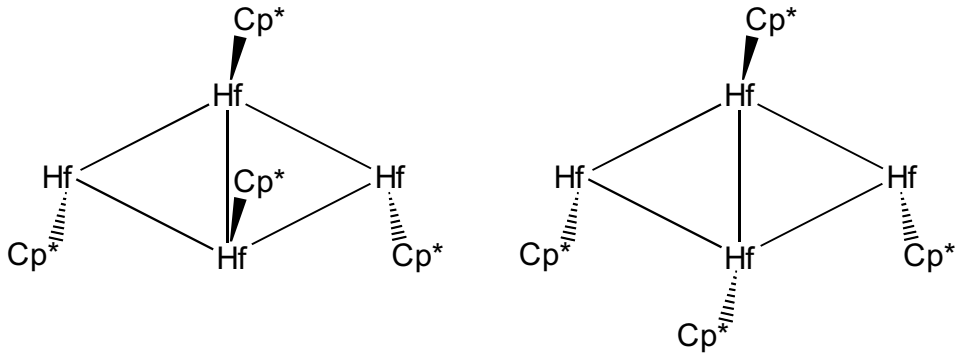


Figure 2.2. Proposed structure of $Cp^*_3Hf_3H_4Cl_5$ (**2.11**)

The polyhydride complex **2.11** could also be obtained by reacting a mixture of 2 equiv of **2.2** and 1 equiv of **2.4** with H_2 (1 bar) in toluene solvent for 48 h (which could possibly circumvent the coformation of Cp^*HfCl_3), but this resulted in a lower isolated yield (35%).

Monitoring the reaction of the dialkyl complex **2.4** with H_2 (benzene-d_6 solvent) by ^{1}H NMR spectroscopy at ambient temperature and pressure revealed the formation of two yellow polyhydride products in a ratio of close to 1:1. The first is the known complex $[Cp^*Hf(H)_2Cl]_4$ (**2.12**), as concluded from the hydride NMR resonances at δ 8.38 and 11.14 ppm[12] and confirmed by its isolation from a reaction on preparative scale. The other hydride species shows hydride resonances

at δ 11.34, 9.68, 8.97, and 6.84 ppm in a 2:2:2:2 ratio, all coupled to each other (as seen from a ^{1}H,^{1}H-COSY spectrum), and which are clearly distinct from those observed for $Cp^*_3Hf_3H_4Cl_5$. In addition, three Cp* resonances in a ratio of 2:1:1 are associated with this species. Formation of Cp^*HfCl_3 could not be detected, indicating that this hydride is also likely to have the stoichiometry $[Cp^*Hf(H)_2Cl]_n$. Attempts to increase the relative amount of this unknown hydride species by performing the reaction at different H_2 pressures (varying from 1.2 equiv to 6 bar) and different reaction times (varying from 4 h to a week), both on NMR and preparative scale, were unsuccessful. The ratio remained approximately 1:1. It is likely that the two species have a similar (tetranuclear) core structure: both show hydride resonances at very low field (δ around 11 ppm), and both are inert to Lewis bases like PMe_3. They possibly represent isomers of $[Cp^*Hf(H)_2Cl]_4$ with different relative positions of the Cp* ligands with respect to the Hf_4 diamond (Figure 2.3); one with a symmetrical structure (δ 8.38 and 11.14 ppm), the structure of which is known from single crystal X-ray diffraction,[12] and one with an asymmetrical structure (δ 11.34, 9.68, 8.97, and 6.84 ppm).



2.12
symmetrical form

2.12
asymmetrical form

Figure 2.3. The two forms of **2.12**.

Monitoring the reaction of the trialkyl complexes **2.5** and **2.6** with H_2 (benzene-d_6 solvent) by ^{1}H NMR spectroscopy at ambient temperature and pressure revealed a fast reaction with H_2, as resonances for free (*n*-propyl)dimethylamine appeared immediately. Nevertheless, resonances attributable to (poly)hydride species could not be observed. Due to the difficulties in obtaining completely pure **2.5** and **2.6**, reactions on a preparative scale have not been performed at this stage.

Reaction of the tetraalkyl complex **2.7** with H_2 both on NMR scale (benzene-d_6 solvent) and preparative scale (toluene solvent) at ambient temperature and pressure resulted in the precipitation of an insoluble black solid. Reaction of the black product with CD_3OD resulted in the formation of (*n*-propyl)dimethylamine-d_1 (GC/MS), indicating that this ligand is still covalently bound to the metal prior to methanolysis. Elemental analysis gave the following values: C 34.74, H 7.45, N 7.24 and Zr 46.58%. The closest stoichiometry to these values is $\{ZrH[(CH_2)_3NMe_2]\}_n$, for which the calculated values are: C 33.67, H 7.35, N 7.85 and Zr 51.15%. This is probably a polymeric species since it is totally insoluble, and the black color is consistent with reduction of Zr^{IV} to a lower valency.

2.3 Attempted synthesis of other hafnium *N,N*-dimethylaminopropyl complexes.

Thus far, the polynuclear Cp*M-polyhydrides (M = Zr, Hf) obtained are of a family with stoichiometry $Cp^*MH_nCl_{3-n}$. For the generation of species Cp^*MH_n it is necessary to have pure, chloride-free precursors for the hydrogenolysis reaction. As the trialkyls **2.5** and **2.6** (see section 2.1) are oils that are difficult to purify, attempts were made to synthesize alternative, crystallizable trialkyl precursors. Salt metathesis and ligand redistribution routes were employed to access the mixed trialkyl complexes $Cp^*HfMe_2[(CH_2)_3NMe_2]$, $Cp^*HfMe[(CH_2)_3NMe_2]_2$ and $Cp^*Hf(CH_2Ph)_2[(CH_2)_3NMe_2]$. However, all attempts to obtain these products in pure form were unsuccessful. Reaction of **2.2** with 2 equiv of MeMgI or MeLi gave predominantly Cp^*HfMe_3 or a mixture of Cp^*HfMe_3 and other methyl compounds. When a similar reaction was performed with 2 equiv of $PhCH_2MgBr$, $Cp^*Hf(CH_2Ph)_3$ was obtained as the main product. An inverted alkylation sequence, reaction of Cp^*HfCl_3 with 2 equiv of MeMgI followed by reaction with $Li(CH_2)_3NMe_2$ or $ClMg(CH_2)_3NMe_2$, was not successful either; the same kind of mixtures were obtained. An attempted ligand redistribution between **2.6** and $Cp^*Hf(CH_2Ph)_3$ did not result in a reaction at room temperature over a period of one week. Reaction of Cp^*HfCl_3 with MeMgI, followed by reaction with 2 equiv of $ClMg(CH_2)_3NMe_2$ did not yield the desired product $Cp^*HfMe[(CH_2)_3NMe_2]_2$, but rather what (based on NMR spectroscopy) is probably a mixture of $Cp^*HfMe_2[(CH_2)_3NMe_2]$, a minor amount of

$Cp^*HfMe[(CH_2)_3NMe_2]_2$ and other unidentified components. It proved impossible to crystallize any of these species selectively from these mixtures.

Reaction of this last mixture with H_2 revealed gradual formation of free (*n*-propyl)dimethylamine and a blue solution, but NMR resonances attributable to a (poly)hydride species could not be seen.

2.4 Conclusions

The hydrogenolysis of pentamethylcyclopentadienyl Zr and Hf *N*,*N*-dimethylaminopropyl dichloride complexes leads to the formation of a well-defined, crystallizable trinuclear hydride species, $Cp^*_3M_3H_4Cl_5$ (with a hydride-to-metal ratio of 1.33H/M). The highly asymmetric trinuclear structure of $Cp^*_3M_3H_4Cl_5$ is rather unusual, but it probably represents the thermodynamically most stable structure, as the complex readily self-assembles in solution via ligand exchange reactions, eliminating a molecule of Cp^*MCl_3. The use of the *N*,*N*-dimethylaminopropyl group appears to aid the formation of this discrete species (unlike the ill-defined polymeric products produced upon hydrogenolysis of other $Cp^*M(alkyl)Cl_2$ compounds), but the (*n*-propyl)dimethylamine itself is not incorporated into the final product. This principle should be more widely applicable in the synthesis of polynuclear polyhydrides of highly electron-deficient metal centers.

Similarly, the hydrogenolysis of the Hf bis(*N*,*N*-dimethylaminopropyl) monochloride complex also leads to the formation of soluble, discrete polyhydride species. In this case $[Cp^*Hf(H)_2Cl]_4$ (2H/Hf) is formed, which appears to exist as two isomers. Interestingly, only one of these (the one with the highest symmetry) was reported to be formed in the hydrogenolysis of Cp*Hf(2,3-dimethyl-1,3-butadiene)Cl,[12] suggesting that there may be some form of kinetic control in the formation of these polyhydrides.

For the synthesis of a putative polyhydride complex "$[Cp^*HfH_3]_n$" (3H/M), a pure, soluble Cp^*HfR_3-type precursor is required. Presently, the complexes $Cp^*M[(CH_2)_3NMe_2]_3$ and derived mixed alkyl complexes $Cp^*Hf[(CH_2)_3NMe_2]Me_2$ could not be prepared in a way that fulfils these criteria. Therefore attempts were made to obtain "$[Cp^*HfH_3]_n$" compounds from complexes with another hydrogenolizable ligand, 2,3-dimethyl-1,3-butadiene. These experiments are described in Chapter 3.

Acknowledgement

I would like to thank dr. A. Ehlers of the Free University (Amsterdam) for performing the DFT calculations on the polyhydride complexes.

2.5 Experimental section

General considerations. All manipulations were carried out under nitrogen atmosphere using standard glovebox, Schlenk, and vacuum-line techniques. Solvents were predried over Na wire, distilled from Na (toluene) or Na/K alloy (Et_2O, pentane, hexane, THF) and stored under nitrogen. Deuterated solvents (C_6D_6, C_7D_8, C_4D_8O; Aldrich) were vacuum transferred from Na/K alloy. Hydrogen gas (AGA 99.9%) was used as purchased. Cp^*MCl_3 (M = Zr, Hf)[21], $Li(CH_2)_3NMe_2$[22] and $Cp^*Zr[(CH_2)_3NMe_2]_2Cl$ (**2.3**)[13] were synthesized according to published procedures. $Me_2N(CH_2)_3MgCl$ was prepared in THF from the corresponding alkyl chloride. NMR spectra were recorded on Varian VXR 300 or Varian Unity 500 spectrometers. The ^1H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances and reported in ppm relative to TMS (δ 0 ppm), *J* is reported in Hz. IR spectra were recorded from Nujol mulls between KBr disks on a Mattson-4020 Galaxy FT-IR spectrometer. Elemental analyses were performed at the Microanalytical Department of the University of Groningen. Found values are the average of two independent determinations.

$Cp^*M[(CH_2)_3NMe_2]Cl_2$ (M = Zr, 2.1; Hf, 2.2). Onto a mixture of solid Cp^*ZrCl_3 (1.75 g, 5.26 mmol) and $Li(CH_2)_3NMe_2$ (0.49 g, 5.26 mmol), which was frozen in liquid nitrogen, 10 mL of THF was condensed. The mixture was allowed to warm up to room temperature and after stirring for 1 h at room temperature the solvent was removed *in vacuo*. Residual solvent was removed by stirring the mixture in 7 mL of pentane, which was subsequently pumped off. The white mixture was extracted twice with 20 mL of pentane. Concentrating the extract and cooling to –60 ºC yielded 1.35 g (3.52 mmol, 67%) of yellow crystalline **2.1**. ^1H NMR (300 MHz, C_6D_6, 20 ºC) : δ 2.67 (m, 2H, NCH_2), 2.47 (s, 6H, NMe_2), 1.91 (s, 15H, C_5Me_5), 1.80 (m, 2H, CH_2), 0.69 (m, 2H, $ZrCH_2$). ^{13}C NMR (75.4 MHz, C_6D_6, 20 ºC) : δ 122.77 (s, Cp* C), 65.23 (t, J = 116.8, $ZrCH_2$), 63.06 (t, J = 135.8, NCH_2), 48.03 (q, J = 137.0, NMe_2), 26.73 (t, J = 126.6, CH_2), 12.18 (q, J = 127.0, Cp* Me). ^1H and ^{13}C NMR assignments were aided by

^{1}H,^{13}C-HSQC 2D NMR spectra. IR: 2710(vw), 1481(vw), 1390(m), 1262(vw), 1248(w), 1231(mw), 1166(m), 1099(m), 1048(m), 1008(vs), 979(s), 905(m), 872(m), 810(w), 773(vs), 723(mw), 640(vw), 593(w), 488(m), 356(mw) cm^{-1}. Anal. Calcd. for $C_{15}H_{27}NCl_2Zr$: C, 46.98; H, 7.10; Cl, 18.49; Zr, 23.79. Found : C, 46.69; H, 7.08; Cl, 18.38; Zr, 23.73.

The same procedure using Cp*$HfCl_3$ (1.71 g, 4.07 mmol) yielded 1.11 g (2.36 mmol, 65%) of white crystalline Cp*Hf[$(CH_2)_3NMe_2$]Cl_2 (**2.2**). ^{1}H NMR (500 MHz, toluene-d_8, 0 ºC) : δ 2.52 (t, 2H, J = 7.0, NCH_2), 2.35 (s, 6H, NMe_2), 1.96 (s, 15H, C_5Me_5), 1.91 (m, 2H, CH_2), 0.57 (t, 2H, J = 8.0, $HfCH_2$). ^{13}C NMR (125.68 MHz, toluene-d_8, 0 ºC) : δ 120.91 (s, Cp* C), 64.44 (t, J = 114.4, $HfCH_2$), 63.69 (t, J = 135.8, NCH_2), 47.69 (q, J = 132.0, NMe_2), 25.17 (t, J = 125.9, CH_2), 11.93 (q, J = 126.7, Cp* Me). ^{1}H and ^{13}C NMR assignments were aided by ^{1}H,^{13}C-HSQC 2D NMR spectra. IR: 2726(m), 2672 (w), 1311(m), 1235(vw), 1169(s), 1155(sh), 1105(m), 1055(m), 1015(s), 974(s), 907(m), 891(w), 870(m), 808(w), 774(s), 723(vs), 593(mw), 488(m) cm^{-1}. Anal. Calcd. for $C_{15}H_{27}NCl_2Hf$: C, 38.27; H, 5.78; N, 2.98; Cl, 15.06; Hf, 37.91. Found : C, 37.95; H, 5.77; N, 2.85; Cl, 14.92; Hf, 37.78.

Cp*Hf[$(CH_2)_3NMe_2$]$_2$Cl (2.4). At –35 ºC, 3.0 mL of a 0.50 M solution of $Me_2N(CH_2)_3MgCl$ in THF was added dropwise to a suspension of Cp*$HfCl_3$ (0.31 g, 0.74 mmol) in 10 mL Et_2O. The mixture was allowed to warm up to room temperature and after 5 h the solvent was removed *in vacuo*. Residual solvent was removed by stirring the mixture in 7 mL of pentane, which was subsequently pumped off. The white mixture was extracted twice with 20 mL of pentane. Concentrating the extract and cooling to –60 ºC yielded 0.20 g (0.38 mmol, 51%) white crystalline **2.4**. ^{1}H NMR (500 MHz, toluene-d_8, –60 ºC): δ 2.50 (br, 1H, CH*H*'), 2.37 (s, 3H, NMe), 2.33 (br, 1H, N-CH*H*'), 2.32 (br, 1H, N-C*H*H'), 2.23 (s, 6H, NMe_2'), 2.15 (br, 1H, C*H*H'), 1.97 (br, 1H, CH*H*), 1.88 (br, 1H, C*H*H), 1.84 (br, 1H, N-CH*H*), 1.83 (s, 15H, C_5Me_5), 1.80 (s, 3H, NMe), 1.59 (br, 1H, N-C*H*H), 0.65 (br, 1H, Hf-CH*H*), 0.48 (br, 1H, Hf-CH*H*'), 0.35 (br, 1H, Hf-C*H*H), 0.11 (br, 1H, Hf-C*H*H'). ^{13}C NMR (125.68 MHz, toluene-d_8, –60 ºC): δ 118.97 (s, Cp* C), 70.09 (t, J = 117.2, $HfCH_2$'), 67.44 (t, J = 130.0, NCH_2'), 64.92 (t, J = 134.0, NCH_2), 54.98 (t, J = 114.7, $HfCH_2$), 47.95 (q, J = 136.8, NMe), 46.06 (q, J = 135, NMe_2+NMe), 29.36 (t, J = 123.3, CH_2'), 24.77 (t, J = 132.3, CH_2), 11.89 (q, J = 126.2, Cp* Me). With 2D NMR experiments (DQCOSY, HSQC and NOESY) the different signals could be assigned to the various CH_2 groups.

Resonances belonging to the non-chelating alkyl group are indicated by a prime ('). IR: 2817(w), 2765(m), 2705(vw), 1400(w), 1317(mw), 1302(w), 1277(vw), 1254(s), 1231(w), 1217(s), 1165(s), 1115(w), 1098(m), 1042(s), 1031(vw), 1007(s), 972(sh), 901(m), 851(s), 802(w), 762(s), 723(mw), 594(s), 552(m), 530(m), 482(m), 467(vw) cm^{-1}. Anal. Calcd. for $C_{20}H_{39}N_2ClHf$: C, 46.06; H, 7.54; N, 5.37; Cl, 6.80; Hf, 34.23. Found: C, 45.90; H, 7.47; N, 5.29; Cl, 6.75; Hf, 34.05.

Cp*M[$(CH_2)_3NMe_2$]$_3$ (M = Zr, 2.5; Hf, 2.6). At –40 ºC, 7 mL of a 0.50 M solution of $Me_2N(CH_2)_3MgCl$ in THF was added dropwise to a suspension of Cp*$ZrCl_3$ (0.30 g, 0.90 mmol) and 0.5 ml (0.59 mmol) 1,4-dioxane in 10 mL Et_2O. The mixture was allowed to warm up to room temperature and stirred overnight. The solvent was removed *in vacuo*. Residual solvent was removed by stirring the mixture in 7 mL of pentane, which was subsequently pumped off. The pale yellow mixture was extracted twice with 50 mL of pentane. Evaporation of pentane yielded **2.5** as a yellow oil in nearly quantitative yield. ^{1}H NMR (500 MHz, C_6D_6, 25 ºC) : δ 2.23 (s, 18H, NMe_2), 2.19 (t, 6H, J = 7.1, NCH_2), 1.86 (s, 15H, C_5Me_5), 1.83 (m, 6H, CH_2), 0.20 (m, 6H, $ZrCH_2$). ^{13}C NMR (125.68 MHz, C_6D_6, 25 ºC): δ 117.96 (s, Cp* C), 67.38 (t, J = 131.2, NCH_2), 56.61 (t, J = 114.1, $ZrCH_2$), 46.45 (q, J = 131.9, NMe_2), 27.63 (t, J = 123.6, CH_2), 11.68 (q, J = 126.2, Cp* Me). ^{1}H and ^{13}C NMR assignments were aided by ^{1}H,^{13}C-HETCOR 2D NMR spectra. IR: 2812(w), 2766(s), 1402(mw), 1362(w), 1316(m), 1254(s), 1204(m), 1167(s), 1098(s), 1040(mw), 1011(mw), 974(s), 947(w), 905(w), 882(m), 847(s), 804(w), 762(s), 583(m), 529(mw), 465(w) cm^{-1}.

The same procedure using Cp*$HfCl_3$ (0.32 g, 0.76 mmol) yielded a pale yellow oil (**2.6**), containing as an impurity 18 mol% of the dialkyl complex **2.4**, as seen by NMR spectroscopy. ^{1}H NMR (500 MHz, C_6D_6, 25 ºC): δ 2.21 (s, 18H, NMe_2), 2.17 (t, 6H, J = 7.6, NCH_2), 1.94 (m, 6H, CH_2), 1.89 (s, 15H, C_5Me_5), 0.13 (m, 6H, $HfCH_2$). ^{13}C NMR (125.68 MHz, C_6D_6, 25 ºC): δ 118.03 (s, Cp* C), 68.32 (t, J = 129.7, NCH_2), 66.49 (t, J = 108.4, $HfCH_2$), 46.30 (q, J = 132.2, NMe_2), 27.48 (t, J = 125.4, CH_2), 11.57 (q, J = 126.4, Cp* Me). ^{1}H and ^{13}C NMR assignments were aided by ^{1}H,^{13}C-HETCOR 2D NMR spectra. IR: 2810(mw), 2766(s), 2625(w), 1402(w), 1364(w), 1316(w), 1296(w), 1256(s), 1231(w), 1215(m), 1167(mw), 1155(w), 1119(w), 1101(w), 1040(s), 1011(s), 982(w), 966(w), 897(w), 849(s), 793(m), 762(w), 594(w), 536(mw), 476(w) cm^{-1}.

M[$(CH_2)_3NMe_2$]$_4$ (M = Zr, 2.7; Hf, 2.8). The procedure is a modification of the synthesis of **2.7** as described in the literature.[16] Onto a solid mixture of $Me_2N(CH_2)_3Li$ (0.89 g, 9.61 mmol) and $ZrCl_4$ (0.56 g, 2.40 mmol) 15 mL of THF was condensed. The mixture was allowed to warm up to room temperature and stirred for 2.5 h. The solvent was removed *in vacuo*. Residual solvent was removed by stirring the mixture in 7 mL of pentane, which was subsequently pumped off. The brown mixture was extracted twice with 20 mL of pentane. Evaporation of pentane yielded 0.99 g (95%) of **2.7** as a brown oil, essentially pure by NMR spectroscopy. ^{1}H NMR (300 MHz, C_6D_6, 25 ºC) : δ 2.23 (s, 18H, NMe_2), 2.19 (t, 6H, J = 7.1, NCH_2), 1.86 (s, 15H, C_5Me_5), 1.83 (m, 6H, CH_2), 0.20 (m, 6H, $ZrCH_2$).

The same procedure using $HfCl_4$ (0.49 g, 1.53 mmol) yielded 0.80 g (100%) of a pale yellow oil (**2.8**) with small amounts of impurities of unknown origin, as seen by ^{1}H NMR spectroscopy (resonances at δ 0.85 and 0.60 ppm in a 1:1 ratio together with some resonances around 2 ppm). ^{1}H NMR (300 MHz, C_6D_6, 25 ºC): δ 2.21 (s, 18H, NMe_2), 2.17 (t, 6H, J = 7.6, NCH_2), 1.94 (m, 6H, CH_2), 1.89 (s, 15H, C_5Me_5), 0.13 (m, 6H, $HfCH_2$).

Zr[$(CH_2)_3NMe_2$]$_2$$Cl_2$ (2.9). A mixture of **2.7** (0.74 g, 1.70 mmol) and $ZrCl_4$ (0.40 g, 1.70 mmol) was dissolved at 0 °C in 15 mL of toluene and stirred for 1.5 h at this temperature. The solvent was removed *in vacuo* at this temperature. Residual solvent was removed by stirring the mixture in 8 mL of pentane, which was subsequently pumped off. The remaining brown solid was washed with 8 mL of pentane. Evaporation of pentane yielded **2.9** as a brown solid (0.83 g, 1.0 mmol, 73%). The product is thermally labile at ambient temperature, releasing *N*,*N*-dimethylpropylamine. ^{1}H NMR (500 MHz, toluene-d_8, 20 ºC) : δ 2.62 (t, 4H, J = 6.5, NCH_2), 2.36 (s, 12H, NMe_2), 1.96 (m, 4H, CH_2), 1.56 (m, 4H, $ZrCH_2$). The spectrum at −60 ºC is essentially the same, but the resonances for NCH_2 and NMe_2 are shifted upfield by about 0.15 ppm. ^{13}C NMR (125.68 MHz, toluene-d_8, –60 ºC): δ 66.16 (t, J = 137.8, NCH_2), 65.96 (t, J = 115.6, $ZrCH_2$), 45.53 (q, J = 136.7, NMe_2), 26.85 (t, J = 125.4, CH_2).

Cp*$_3$$Hf_3H_4Cl_5$ (2.11). A solution of **2.2** (0.77 g, 1.64 mmol) in 10 mL of toluene was stirred at room temperature in the dark under H_2 (1 atm) for two days. The pale yellow solution was concentrated and slow diffusion of 15 mL hexane into the solution gave 0.37 g (0.33 mmol, 80%) of white crystalline **2.11**. ^{1}H

NMR (500 MHz, toluene-d_8, –60 ºC): δ 9.17 (m, 1H, H_A), 8.46 (m, 1H, H_B), 7.71 (m, 1H, H_C), 4.63 (m, 1H, H_D), 2.26 (s, 15H, C_5Me_5), 2.14 (s, 15H, C_5Me_5), 1.90 (s, 15H, C_5Me_5); hydride couplings : J_{AB} = 8.3, J_{AC} = 8.9, J_{BD} = 4.3, J_{AD} = 2.1, J_{BC} = J_{CD} = 0 (determined by selective decoupling experiments). Anal. Calcd. for $C_{30}H_{49}Cl_5Hf_3$: C, 32.10; H, 4.40; Cl, 15.79; Hf, 47.71. Found: C, 32.11; H, 4.28; Cl, 15.91; Hf, 47.42.

For comparison, data for the Zr analogue **2.10** are given[13]: ^{1}H NMR (300 MHz, toluene-d_8, –50 ºC): δ 4.23 (m, 1H, H_A), 3.92 (m, 1H, H_B), 2.96 (m, 1H, H_C), 2.21 (s, 15H, C_5Me_5), 2.10 (s, 15H, C_5Me_5), 1.86 (s, 15H, C_5Me_5), 0.88 (1H, H_D); hydride couplings : J_{AB} = 9.9, J_{AC} = 10.6, J_{BD} = 6.2, J_{AD} = 3.3, J_{CD} = 1.5, J_{BC} = 0 (determined by selective decoupling experiments).

Hydrogenolysis of Cp*Hf[(CH$_2$)$_3$NMe$_2$]$_2$Cl. A typical experiment proceeded as follows: A solution of **2.4** (0.45 g, 0.86 mmol) in 10 mL of toluene was stirred at room temperature in the dark under H_2 (1 atm) for two days. The yellow solution was concentrated to about 2 mL and after cooling to –30 ºC, 0.09 g of yellow crystalline material was obtained. This consists of the known [Cp*Hf(H)$_2$Cl]$_4$ (**2.12**) as seen by hydride resonances at δ 11.14 and 8.38 ppm,[12] and a hydride complex which is proposed to be an isomer of [Cp*Hf(H)$_2$Cl]$_4$ with lower molecular symmetry. A reaction on NMR tube scale (C_6D_6 solvent) showed release of the free amine and formation of both hydride species in a ratio of close to 1:1. Asymmetrical [Cp*Hf(H)$_2$Cl]$_4$: ^{1}H NMR (500 MHz, benzene-d_6, 25 ºC): δ 11.34 (m, 2H), 9.68 (m, 2H), 8.97 (m, 2H), 6.84 (m, 2H), 2.34 (s, 30H, C_5Me_5), 2.31 (s, 15H, C_5Me_5), 2.23 (s, 15H, C_5Me_5).

Hydrogenolysis of Zr[(CH$_2$)$_3$NMe$_2$]$_4$. A solution of **2.9** (0.97 mmol, 0.42 g) in 8 mL of toluene was stirred at room temperature under H_2 (1 atm) for 24 h. A black solid deposited from a brown solution during the reaction. After evaporation of the solvent, the black solid was washed with 6 mL of pentane. Hereafter, 0.12 g of a black powder was isolated, which was insoluble in common NMR solvents and which was analyzed by elemental analysis to be approximately [ZrH(CH$_2$)$_3$NMe$_2$]$_n$. Anal. Calcd. for $C_5H_{13}NZr$: C, 33.67; H, 7.35; N, 7.85; Zr, 51.15. Found: C, 34.74; H, 7.45; N, 7.24; Zr, 46.58.

Attempted synthesis of Cp*HfR$_x$[(CH$_2$)$_3$NMe$_2$]$_{3-x}$ (R = Me, CH$_2$Ph). A typical experiment, for the attempted preparation of Cp*HfMe$_2$[(CH$_2$)$_3$NMe$_2$],

proceeded as follows: At –30 ºC, 0.50 mL of a 0.88 M solution of MeLi in Et_2O was added dropwise to a suspension of **2.2** (0.09 g, 0.19 mmol) in 7 mL Et_2O. The mixture was allowed to warm up to 0 ºC and after 1 h the solvent was pumped off. Residual solvent was removed by stirring the mixture in 6 mL of pentane, which was subsequently pumped off. The white mixture was extracted twice with 20 mL of pentane, which was subsequently pumped off. The remaining white solid was investigated by NMR spectroscopy.

A representative experiment involving the reverse alkylation sequence, for the attempted preparation of $Cp^*HfMe[(CH_2)_3NMe_2]_2$, proceeded as follows: At –40 ºC, 0.27 mL of a 1.48 M solution of MeMgI in Et_2O was added dropwise to a suspension of Cp^*HfCl_3 (0.14 g, 0.33 mmol) in 5 mL Et_2O. The mixture was allowed to warm up to 0 ºC and stirred for another 2.5 h. After recooling to –40 ºC, 0.95 mL of a 0.74 M solution of $Me_2N(CH_2)_3MgCl$ in THF was added dropwise to the solution. After 30 minutes of stirring at 0 ºC the solvent was removed *in vacuo*. Residual solvent was removed by stirring the mixture in 5 mL of pentane, which was subsequently pumped off. The white mixture was extracted twice with 10 mL of pentane, which was subsequently pumped off. This yielded a white solid that was investigated by ^1H NMR spectroscopy. This suggested that a mixture is formed consisting of $Cp^*HfMe_2[(CH_2)_3NMe_2]$, a small amount of $Cp^*HfMe[(CH_2)_3NMe_2]_2$ and other unknown species.

X-ray structure determination of 2.11. A suitable crystal of **2.11** was glued on top of a glass fiber by using inert-atmosphere handling techniques and transferred into the cold nitrogen stream on an Enraf-Nonius CAD-4F diffractometer (graphite-monochromated Mo-K$\bar{\alpha}$ radiation, λ = 0.71073, $\Delta\omega = 0.90 + 0.34$ tg θ). Accurate cell parameters and an orientation matrix were determined from the setting angles (SET4)[23] of 22 reflections in the range of $18.19^o < \theta < 20.62^o$. Reduced cell calculations did not indicate any higher lattice symmetry.[24] Crystal data and details on data collection and refinement are presented in Table 2.3. Intensity data were corrected for Lorentz and polarization effects, and for absorption. The structures were solved by Patterson methods and subsequent difference Fourier techniques (DIRDIF).[25] All calculations for **2.11** were performed on a HP9000/735 computer with the program packages SHELXL[26] (least-squares refinements) and PLATON[27] (calculation of geometric data and the ORTEP illustrations). One of the three Cp^* ligands is rotationally disordered: the electron density of the outer carbon atoms (C26-C30) appeared to be spread out.

Attempts to refine a disorder model with discrete C-positions with fractional occupation in this region failed; so in the final refinement these atoms showed unrealistic displacement parameters. The hydrogen atoms were included in the final refinement riding on their carrier atoms with their positions calculated by using hybridization at the C atom as appropriate with U_{iso} = 1.5 x U_{equiv} of their parent atom, where values U_{equiv} are related to the atoms to which the H atoms are bonded. The methyl-groups were refined as rigid groups, which were allowed to rotate free. The positions of the hydride ligands could not be unequivocally determined from the final difference Fourier map.

Table 2.3. Crystallographic data for $Cp^*_3Hf_3H_4Cl_5$ (**2.11**).

chem formula	$C_{30}H_{49}Cl_5Hf_3$	μ (Mo Kα) (cm^{-1})	92.5
M_r	1122.45	F(000)	1060
cryst syst	triclinic	temp (K)	130
color, habit	white, plate	θ range (deg)	1.47-27.5
size (mm)	0.12x0.38x0.48	ω scan width (deg)	0.90+0.34 tg θ
space group	*P*-1	data collected (h,k,l)	-11:11,-14:0,-22:22
a (Å)	9.029(1)	min and max transm	0.0579, 0.4111
b (Å)	11.214(1)	no. of rflns collected	8737
c (Å)	17.449(2)	no. of indpndt rflns	8065
α (deg)	88.912(9)	observed rflns	7308 ($F_o \geq 4\sigma(F_o)$)
β (deg)	83.370(8)	R(F) (%)	5.89
γ (deg)	88.690(8)	*w*R(F^2) (%)	15.6
V ($Å^3$)	1754.2(3)	GOF	1.013
Z	2	weighting a,b	0.0924,49.26
D_{calc} (g cm^{-3})	2.125	params refined	358

DFT calculations on $(C_5H_5)_3M_3H_4Cl_5$ (M = Zr; Hf). The calculations were carried out using the parallelized Amsterdam-Density-Functional (ADF) program.[28] For the geometry optimisations the MOs were expanded in a large, uncontracted set of Slater type orbitals (STOs) containing polarization functions. The used TZP basis set is of triple-ζ quality for all atoms and has been augmented with one set of 4p functions for each transition metal atom, and one set of d-polarization functions for each main group atom.[29] The 1s core shell of carbon and the 1s2s2p core shells of chlorine were treated by the frozen-core (FC) approximation. The metal centers were described by an uncontracted triple-ζ STO basis set for the outer ns, np, nd, (n+1)s, (n+1)p orbitals for zirconium and in the

case of hafnium also for the 4f orbitals, whereas the shells of lower energy were treated by the frozen core approximation. An auxiliary set of s, p, d, f, and g STOs, centered on all nuclei, was used to fit the molecular density and to represent the Coulomb and exchange potentials accurately in each self-consistent field (SCF) cycle.[30] The numerical integration and the calculation of the VDD charges was done with the scheme developed by te Velde *et al.*[31]

All calculations were performed at the NL-SCF level, using the local density approximation (LDA) in the Vosko-Wilk-Nusair parametrization[32] with nonlocal corrections for exchange[33] and correlation.[34] All geometries were optimized using the analytical gradient method implemented by Versluis and Ziegler.[35] Relativistic effects were taken into account by the ZORA approximation.[36]

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